SCOVELL

A Modification of the Kjeldahl Method for the Determination of Total Nitrogen Including Nitric Nitrogen

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A MODIFICATION OF THE KJELDAHL METHOD FOR THE DETERMINATION OF TOTAL NITROGEN INCLUDING NITRIC NITROGEN

BY

MELVILLE AMASA SCOVELL

THESIS

FOR THE

DEGREE OF DOCTOR OF PHILOSOPHY

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OF Doctor of Philosophy

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A MODIFICATION OF THE KJELDAHL METHOD FOR THE DETERMINATION OF TOTAL NITROGEN, INCLUDING NITRIC NITROGEN.

By M. A. Scovell.

The Kjeldahl Method for the determination of nitrogen came in at an opportune time. Kjeldahl* described his method in 1883. This was just prior to the organization of most of the American Experiment Stations. Naturally, the first and most important work for the Stations to take up was feeding and digestion experiments on animals, and the study of soil fertility, and more especially to this end the analyses of commercial fertilizers. Founded on the suggestion of Liebig, Ville and others, commercial fertilizers were being manufactured to supply phosphorus, potassium and nitrogen to soils which had been more or less depleted of these elements by continued cropping. Recognizing that their value largely depended on the amount and availability of these elements, laws were being passed both in this country and Europe to compel manufacturers of fertilizers to guarantee the percentages of these elements. The enforcement of such laws fell either upon the Experiment Stations or on the State Agricultural Departments. One of the greatest difficulties at once encountered was the want of methods of analysis which would give uniform and accurate results and insure rapid work, and especially was this true in regard to a method for the determination of nitrogen. In this country the official chemists organized themselves into an association known as the Association of Official Agricultural Chemists of the United States. Their

* Zeit. Anal. Chem. 22, 366.

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first work was mainly to compare methods in order to obtain accurate and uniform results. As late as 1885, this association was without an accepted method for the determination of nitrogen. The committee appointed to consider the report of the Committee on Nitrogen stated that the discrepancies were so large as to make it inadvisable to recommend any method at this time for the determination of nitrogen.

The so-called Absolute or Copper Oxide Method gave, with careful and painstaking labor, theoretical results. But it was evident that if chemistry were to play its part in the now rapidly advancing agricultural science, methods of analysis, accurate, simple and rapid of execution, must first be devised. It was in this period that so many chemists spent largely of their time in studying chemical methods.

In the determination of nitrogen the Soda-lime Method was tedious and difficult of operation, the combustion tubes often broke which caused the loss of much time, and the length of time in making a determination was a serious drawback. And, furthermore, this method was not applicable where nitrates were present which is often the case in fertilizers. The great length of time it takes to estimate nitrogen by the Dumas or Absolute Method was cause for looking for a simpler and more rapid method. A single analysis by either the Dumas or the Will and Varrentrapp Methods, even by chemists of many years experience, and with all improvements suggested by the combined labor of many workers, taxed the skill of experienced chemists for many hours.

The Ruffle Method received considerable attention, especially by the Association of Official Chemists. In some hands it worked

well, but as to length of time in manipulation, loss of results, breakage of tubes, etc., it had the same faults as the Soda-lime Method. Where nitrates were present in small quantities, it seemed to work well, but on pure nitrates it failed to give theoretical results. In estimating pure potassium nitrate by the Ruffle Method, the writer obtained the following results:

1.	11.12 %	nitrogen.
2.	12.56 "	"
3.	12.04 "	"
4.	11.68 "	"
Average	11.85 "	"
Theory	13.85 "	"

On pure sodium nitrate the results were:

1.	14.61 %	nitrogen.
2.	15.42 "	"
3.	13.27 "	"
4.	15.08 "	"
5.	15.56 "	"
Average	14.79 "	"
Theory	16.67 "	"

From 1886 to 1891 the writer spent much of his time in the laboratory studying a method for the determination of nitrogen. The method sought was one that would be applicable to all the ordinary sources of nitrogen; to give theoretical results on pure salts; and rapid in execution. A modification of the Kjeldahl Method promised the most attractive field for investigation. The

Kjeldahl Method was all that could be desired so far as rapidity of execution was concerned, but at this time it was not applicable in all cases of nitrogen determinations, and especially was this true when nitrates were present.

Many investigators studied this method to make it applicable to nitric nitrogen. Kjeldahl suggested that if sug r were added in the manipulation the reducing power of the sugar would change the nitrate to ammonia. But Ashboth[a] found that sugar did not reduce all of the nitrates. He suggested and tried benzoic acid in place of sugar. Jodlbaur[b] found that the benzoic acid method gave results far too low when nitrates were present. This author suggested the use of phenol in place of benzoic acid. Kjeldahl had observed that in his process the nitrogen of amines was readily converted into ammonia. Jodlbaur, by the use of phenol, endeavored to convert the nitric acid into nitro phenol, then by zinc as a reducing agent to convert the nitro-compounds into amines. For this purpose he treated about 0.5 grams of a nitrate with 20 c.c. of concentrated sulphuric acid and 2 1/2 c.c. phenol sulphonic acid (100 c.c. containing 50 grams of phenol), and then with 2 or 3 grams of zinc dust and a few drops of platinic chloride solution.

Stutzer and Reitmaier[c] found that the Jodlbaur Method did not give good results when the percentage of nitrates was large in the substance to be determined and when the substance to be examined was a pure nitrate. They suggested that loss of nitrogen followed when phenol sulphonic acid was allowed to act upon compact masses of

(a) Chem. Central. 17, 161.

(b) Chem. Centralb. 17, 4[illegible]3.

(c) Anal. Chem. 7, 4.

the substance. To obviate this difficulty they dissolved the material to be analyzed in about 25 c.c. of water and evaporated this to dryness in an air bath. This evaporation was conducted in a Kjeldahl flask. They claimed that by this method the nitrates were evenly distributed when the phenol sulphonic acid was added. After standing for a few minutes 2 to 3 grams of zinc dust and a few drops of metallic mercury were added and the mixture boiled until oxidation took place. A great number of analyses were made by this method and the results recorded were quite accurate when nitrates were not in too large quantities in the substance analyzed. The heat generated by the addition of the nitro phenol to nitrates almost invariably causes the loss of some of the nitrogen. Great care must be taken that the reaction be not too great. Not only is it necessary to dissolve the substance and evaporate to dryness as suggested by Stutzer and Reitmaier but it is essential that the Kjeldahl flask be very cold when the sulphuric acid containing the phenol is added, and it is better to keep the flask in ice water. Often with these precautions it is quite difficult to get theoretical results. Otto Forester[a] observes that the flask must be cooled or the results will be low. A. Stutzer[b] mixed 2 to 3 grams of ignited gypsum with the nitrate, in order to divide and dilute the nitrate, to prevent too vigorous reaction and thereby preventing loss. Still he finds it necessary to cool the flask.

In the writer's hands the Jodlbaur Method, using the precautions suggested by various chemists, gave the following results on pure

(a) Chem. Zeit. 12, 1555 and 13, 229.

(b) Landw. Ver. Sta. 35, 445 -448.

potassium nitrate:

1. 13.70 % nitrogen.
2. 13.60 " "
3. 13.65 " "
4. 13.75 " "
5. 13.74 " "
6. 13.76 " "
7. 13.62 " "
8. 13.67 " "
9. 13.68 " "

Average 13.69

Theory 13.85

The average is 0.16 % below the theoretical.

On pure sodium nitrate the following results were obtained:

1. 16.40 % nitrogen.
2. 16.52 " "
3. 16.57 " "
4. 16.47 " "
5. 16.49 " "

Average 16.49

Theory 16.67

The average is 0.18 % below the theoretical.

This method was next tried on mixtures containing a small quantity of nitric nitrogen. First, on a mixture of acid phosphate and sodium nitrate containing 3.28 % of nitrogen. Nitrogen found 3.10 % and 3.30 %; average, 3.20 %. Another sample contained acid phosphate, blood and pure sodium nitrate, containing 3.04 %

of nitrogen. Nitrogen found 2.94 %, 2.92 % and 2.92 %; average 2.93 %. Another sample containing acid phosphate, blood, sulphate of ammonia and pure sodium nitrate was analyzed by this method. Nitrogen found 2.49 %, 2.49 % and 2.52 %; average, 2.50 %; the sample containing 2.58 % of nitrogen according to the separate determinations of blood, sulphate of ammonia and pur sodium nitrate added.

Farrington[a] compared this method with the Absolute Copper Oxide Method on 40 different samples of commercial fertilizers containing total nitrogen from 2 1/2 to 6 1/2 %, of which 1/2 to 2 1/2 % were in the form of nitrates. The greatest variation was 0.24 %. 7 % of the samples varied between 0.20 and 0.24 %.

Being convinced that by the use of phenol the reaction was so vigorous as to cause loss of nitrogen even when precautions were taken to keep the mixture cool, and by the addition of water and subsequent evaporation before adding the sulphuric acid, the method became prolonged and tedious, the writer began an investigation to find if possible some other substance which could be used in place of phenol and which would readily form nitro-compounds at low temperatures with nitrates dissolved in concentrated sulphuric acid. After a careful research with which certain organic compounds formed nitro-compounds, the writer was lead to believe that salicylic acid was the substance sought. It is a higher oxidized product than phenol.

The first experiments made with salicylic acid were on chemically pure potassium nitrate. This contained 0.07 % of water.

(a) Connecticut Station Report, 1887, page 126.

The method was as follows: 0.7 gram of potassium nitrate was put into a Kjeldahl flask and dissolved in 30 c.c. of sulphuric acid. 2 grams of salicylic acid were added and the contents shaken, then 3 grams of zinc dust were gradually added and 2 drops of platinic chloride solution. The whole was first gradually heated until danger of frothing was over, then the temperature increased until the liquid boiled rapidly in the flask. After vigorous reaction ceased, 0.7 gram of mercuric oxide was added and the boiling continued until the liquid was nearly colorless; allowed to cool somewhat, and then powdered potassium permanganate was gradually added until the greenish or purple color remained. The results obtained were highly satisfactory and are given below:

1. 13.60 % nitrogen.
2. 13.78 " "
3. 13.85 " "
4. 13.82 " "
5. 13.83 " "
6. 13.92 " "
7. 13.88 " "
8. 13.80 " "
9. 13.84 " "
10. 13.80 " "
11. 13.85 " "
12. 13.78 " "
13. 13.82 " "
14. 13.77 " "
15. 13.79 " "
16. 13.80 " "

17. 13.84 % nitrogen.

Average 13.80

Theory 13.83

On pure sodium nitrate, the following results were obtained:

1. 16.70 % nitrogen.
2. 16.58 " "
3. 16.62 " "
4. 16.65 " "
5. 16.68 " "
6. 16.68 " "

Average 16.65

Theory 16.67

Next, several determinations were made on a sample of pure nitrate of soda containing sugar, with the following results:

1. 3.37 % nitrogen.
2. 3.38 " "
3. 3.38 " "
4. 3.37 " "
5. 3.36 " "
6. 3.40 " "
7. 3.36 " "
8. 3.38 " "
9. 3.38 " "
10. 3.36 " "

Average 3.37

The Absolute Method gave 3.38 % nitrogen.

A number of determinations were made on samples sent out by Dr. Gascoyne, then Chairman of the Committee on Nitrogen of the Association of Official Agricultural Chemists in 1887. The last of these analyses were made a year or more after the samples were sent to our laboratory. The samples were described as follows:

1. Dried blood containing 13.82 % of nitrogen by the Absolute Method.
2. Acid phosphate and dried blood containing 2.76 % of nitrogen.
3. Acid phosphate, dried blood and cotton seed meal containing 3.30 % of nitrogen.
4. Acid phosphate and chemically pure nitrate of soda containing 3.28 % of nitrogen.
5. Acid phosphate, dried blood and chemically pure nitrate of soda containing 3.04 % of nitrogen.
6. Acid phosphate, dried blood, chemically pure sodium nitrate and chemically pure ammonium sulphate, containing 2.58 % of nitrogen, 1.06 % of nitrogen from ammonium salts, 0.82 % from nitrates and 0.70 % from organic material.

Samples Nos. 4, 5 and 6 were determined by the salicylic acid method with the following results:

	Per cent. of nitrogen found.		
	Sample 4.	Sample 5.	Sample 6
1.	3.21	2.97	2.55
2.	3.32	2.99	2.61
3.	3.30	3.05	2.54
4.	3.27	3.02	2.57

	Per cent. of nitrogen found.		
	Sample 4.	Sample 5.	Sample 6.
5.	3.30	3.02	2.59
6.	3.27	2.97	2.58
7.	3.29	3.01	2.58
8.	3.30	3.00	2.60
9.	3.26	3.00	2.57
10.	3.27	2.97	2.58
11.	3.28	---	----
Average	3.28	3.00	2.58

On samples Nos. 1, 2 and 3 determinations were made with and without salicylic acid for the purpose of ascertaining whether salicylic acid retarded the oxidation or in any other way had any influence on the Kjeldahl Method in the determination of nitrogen in organic substances. Results by the Kjeldahl Modified Method:

	Per cent. of nitrogen found.		
	Sample 1.	Sample 2.	Sample 3.
1.	13.70	2.70	3.26
2.	13.78	2.78	3.25
3.	13.84	2.80	3.28
4.	13.80	---	3.28
Average	13.78	2.76	3.27

Results by Kjeldahl Method:

1.	13.78	2.85	3.24
2.	13.74	2.77	3.29
3.	13.79	2.80	3.26
Average	13.77	2.81	3.26

Dr. Gascoyne, in 1887, then Chairman of the Committee on Nitrogen, among other recommendations, made the following recommendation in regard to this method:

> "That, while on account of want of experience of the members of this Association in the use of the Salicylic Acid Modification of the Kjeldahl Method, as recommended by Prof. Scovell, the Committee does not feel authorized to recommend its adoption as an Official Method, but desire to present it to the careful consideration of the Association, in the belief that its simplicity and adaptability to all the contingencies of the fertilizer analysis are such as to render advisable its adoption and use."

At the same meeting a preliminary paper[a] was read by the writer on his method for Nitrogen Determination, and therafter, by a vote of the Association, the method was adopted as the Official Method of the Association.

As Chairman, in 1888, of the Committee on Methods of Nitrogen Determintaion of the Association of the Official Agricultural Chemists, the writer sent out, among other samples, chemically pure potassium nitrate and various laboratories reported results on this sample by the Salicylic Acid Method for the determination of nitrogen[b] Six laboratories reported an average of 13.80 % of nitrogen; the lowest being 13.73 %; the highest 13.86 %. Dr. Jenkins of Connecticut

(a) Bulletin 16, page 61. Div. of Chemistry, U. S. Dep't of Agr.

(b) Bulletin 19. Div. of Chemistry, U. S. Department of Agriculture, page 47.

obtained 13.55 % of nitrogen on the same sample, using phenol in place of salicylic acid. The average of five laboratories, using the Ruffle Method, was 13.38 %.

Dr. E. B. Voorhees[a] of the New Jersey Experiment Station compared in the case of 19 fertilizers the results obtained by the method described by the writer with those obtained by the Absolute Method. The results are herewith given.

> "The modification of Kjeldahl's method, as described by Prof. M. A. Scovell, in the report of the proceedings of the Annual Convention of Official Agricultural Chemists for 1887, was used. The method was found to be reasonably rapid, and no difficulty was experienced in securing results that compared very favorably with those obtained by the Absolute Method. The average determintations of 19 samples show that the percentages of nitrogen are almost identical, the average difference by both methods being one-hundredth of one per cent. The Absolute Method used in this laboratory, is described in detail in the report of the Connecticut Station for 1879. Errors in this method, due to reagents and manipulation, are determined previous to actual work; reagents sufficient for the whole number of determintations to be made are thoroughly mixed, three determinations are made in the usual manner, the gas

(a) Report of New Jersey Experiment Station, 1887, page 169.

measured, and the average of the volume found deducted from the total secured in each analysis. "

"A COMPARISON OF METHODS FOR THE DETERMINATION OF ALL FORMS OF NITROGEN CONTAINED IN FERTILIZERS.

Station Number	Percentage of Nitrogen Kjeldahl modified by Scovell	Percentage of nitrogen Absolute Method.
1769	2.45	2.54
1807	2.64	2.50
1843	2.28	2.26
1844	3.11	3.05
1845	1.92	1.89
1873	4.09	4.08
1900	3.80	3.83
1958	1.98	1.94
1970	2.57	2.59
1991	1.65	1.72
1999	3.03	3.09
2029	1.56	1.53
2049	5.23	5.36
2052	2.93	3.00
2065	4.24	4.28
2075	4.10	3.96
2098	3.19	3.06
2117	1.97	1.87
2118	1.29	1.27 "

1910	.4	.04
1907	.6	.06
1904	.8	.08
1901	1.1	1.00
1898	1.3	1.00
1895	.9	.08
1892	1.0	1.00
1889	1.2	1.00
1886	1.4	1.00
1883	1.6	1.00
1880	1.8	1.00
1877	2.0	2.00
1874	2.2	2.00
1871	2.4	2.00
1868	2.6	2.00
1865	2.8	2.00
1862	3.0	3.00
1859	3.2	3.00
1856	3.4	3.00
1853	3.6	3.00
1850	3.8	3.00

The greatest difference is 0.14 %; the average difference. 0.06 %. In 8 cases the Absolute Method gave an average of 0.05 % more nitrogen In 11 cases the Modified Kjeldahl Method gave on the average of 0.06 % more nitrogen.

Continuing the work, in 1888, the writer made a number of determinations by his method on samples containing chlorides as well as nitrates. It had been stated in the case of the Phenol Kjeldahl Method that in the presence of chlorides loss of nitrogen occurred. For this purpose two samples were prepared. Sample No. 1 contained sodium nitrate and sodium chloride; calculated per cent. of nitrogen being 15.91. Sample No. 2 contained sodium nitrate, cotton seed meal, ammonium sulphate, acid phosphate and potassium chloride; the calculated per cent. of nitrogen being 3.55. The following results were obtained:

	Sample No. 1.	Sample No. 2.
1.	15.83	3.54
2.	15.90	3.52
3.	15.87	3.55
4.	15.85	3.54
5.	15.89	

In the Annual Report of the New Jersey Agricultural Experiment Station, 1888, Dr. Voorhees[a] gives the results of analyses by the Modified Kjeldahl and the Absolute Methods of 42 fertilizers containing nitrates. In these the total nitrogen varied from 0.67 to 7.4 %. The following gives the results in detail:

(a) Report N. J. Exp't Station, 1888, page 131.

"The modification of Kjeldahl's method and the Absolute Method, as described in the report for 1887, were used in all samples of complete fertilizers containing nitrates that were analyzed by the Station during the past season. The average determinations of 42 samples show that the percentages of nitrogen secured were almost identical, the average difference by the two methods being less than two-hundredths of one per cent.

Blank determinations are always made, and the results are modified by the amount of the constant error due to re-agents, etc.

A COMPARISON OF METHODS FOR THE DETERMINATION OF ALL FORMS OF NITROGEN IN FERTILIZERS.

Station Number.	Percentage of nitrogen Kjeldahl modified by Scovell.	Percentage of nitrogen. Absolute Method.
2157	2.68	2.73
2164	3.21	3.25
2171	2.67	2.51
2276	3.67	3.81
2282	2.24	2.31
2284	2.40	2.37
2298	4.54	4.56
2316	2.14	2.02
2329	3.76	3.81
2348	3.10	2.99
2361	2.76	2.67
2378	3.14	3.26
2380	4.05	4.18
2384	4.17	4.27 "
2385	3.93	4.05

Station Number.	Percentage of nitrogen Kjeldahl modified by Scovell	Percentage of nitrogen Absolute method.
2418	7.33	7.40
2425	3.68	3.70
2436	3.78	3.80
2440	3.56	3.51
2445	1.71	1.68
2447	3.78	3.78
2448	2.88	2.90
2450	2.25	2.28
2469	4.27	4.34
2472	2.72	2.73
2504	5.31	5.41
2514	4.13	4.05
2532	1.69	1.59
2535	3.75	3.66
2538	2.72	2.76
2561	3.30	3.31
2583	0.92	0.86
2601	0.79	0.67
2608	2.05	2.17
2618	4.02	3.98
2623	2.63	2.62
2625	2.02	2.12
2638	4.92	5.07
2650	2.40	2.37
2669	0.92	0.96
2673	3.55	3.52
2675	2.52	2.58

The average difference is 0.02 %.

During the many analyses made by this modified method, the writer noticed that on pure nitrates there was apparently a slight loss of nitrogen in adding the zinc dust. This was also a tedious part of the operation as the zinc dust had to be added gradually. Finely granulated zinc dust was tried, but in such cases the results were invariably low. In our laboratory it was found that results were lower when using chemically pure zinc dust instead of the commercial article. An investigation showed that the commercial zinc dust which we had hitherto been using contained some zinc sulphide. This suggested to the writer that hydrogen sulphide might complete the reduction as well if not better than nascent hydrogen. Working on this theory, Prof. Peter and the writer together made a series of experiments[a], using zinc dust in one set of experiments and zinc sulphide in another set. The results on pure potassium nitrate, containing a trace of water, containing 13.83 % of nitrogen were as follows:

	With 3 grams zinc dust. % nitrogen.	With 2 grams Zinc sulphide % nitrogen.
1.	13.76	13.78
2.	13.71	13.77
3.	13.79	13.80
4.	13.78	13.79
5.	13.77	13.83
6.	13.77	13.80
7.	13.69	13.85
8.	13.79	13.80
9.	13.79	13.72
10.	----	13.85
Average	13.76	13.80
Theory	13.83	13.83
Loss	0.07	0.03

(a) Bul. 24, page 91, Div. of Chem., U. S. Dep't of Agr.

On pure sodium nitrate:

	With 3 grams zinc dust. % nitrogen.	With 2 grams zinc sulphide. % nitrogen.
1.	16.36	16.41
2.	16.41	16.44
3.	16.40	16.41
4.	16.42	16.41
5.	---	16.41
6.	---	16.39
Average	16.40	16.41
Theory	16.47	16.47
Loss	0.07	0.06

Dr. Voorhees[a], Reporter on Nitrogen for 1890 of the Association of Official Agricultural Chemists, has this to say in regard to the substitution of zinc sulphide in place of zinc dust.

> "A practical test of this method was also made at the New Jersey Station, where thirty three samples of commercial fertilizers containing nitrate nitrogen, ranging from 0.1 to 2.62 %, were duplicated by the official Kjeldahl for samples containing nitrates and by the suggested modification.

(a) Bulletin 28, page 14, Division of Chemistry, U. S. Department of Agriculture.

2 grams salicylic acid and 2 grams zinc dust. % nitrogen.	1 gram salicylic acid and 2 grams zinc sulphide. % nitrogen.	2 grams salicylic acid and 2 grams zinc dust. % nitrogen.	1 gram salicylic acid and 2 grams zinc sulphide. % nitrogen.
3.51	3.63	4.96	4.94
3.51	3.59	3.03	2.99
2.53	2.50	2.69	2.70
4.21	4.24	4.21	4.26
4.36	4.32	4.06	4.07
3.03	2.91	1.90	1.88
3.97	4.03	3.22	3.21
2.69	2.78	1.85	1.83
2.32	2.17	4.12	4.09
3.03	3.00	1.10	1.06
4.55	4.56	1.45	1.39
3.54	3.62	2.91	2.85
3.31	3.31	1.32	1.24
1.25	1.31	2.82	2.78
3.16	3.04	2.80	2.74
2.41	2.38	4.56	4.56
3.42	3.34	3.18	3.30
3.13	3.08	--	--

The results were highly satisfactory. The difference in duplicates ranged from nothing to 0.12 of 1 %, with an average difference on the whole number of 0.02 of 1 %."

The advantage of zinc sulphide over zinc dust is: First, the liability of the loss of nitrogen is not so great. Second, the zinc sulphide can be added all at once, and therefore, it is less troublesome and more rapid than when zinc dust is used. Third, the oxidation is more rapid, and as less salts are present the distillation is more quiet.

In 1893 sodium thiosulphate was substituted for zinc sulphide as the reducing agent in this method, not because better results were obtained, but because it was found to be difficult to get commercial zinc sulphide free from ammonia. The comparative results obtained by the different chemists using these two reducing agents were slightly in favor of zinc sulphide[a].

Otto Foerster[b] gives the following as the reaction when sodium thiosulphate is used:

$$4HNO_3 + 4H_2SO_4 + Na_2S_2O_3 = 4HO.NO_2.SO_2. + 2NaHSO_4 + 3H_2O.$$

But it would be interesting to know whether hydrogen sulphide which is also formed when salicylic acid and strong sulphuric acid and nitrates are mixed, does not play at least a part in the reduction of the nitro into the amido compounds.

The theory of the process by which salicylic acid converts nitrates to ammonia is as follows:

1. When salicylic acid and sulphuric acid are added to a nitrate, the sulphuric acid takes up water and one of the hydrogen

(a) Bul. 38, pages 34 and 35, Div. of Chemistry, U. S. Dep't Agr.

(b) Zeit. Ana. Chem. 1889, page 422.

elements of the salicylic acid is replaced by NO_2, forming nitro salicylic acid. This reaction takes place without heat. It is probably mononitro and not dinitro salicylic acid that is formed. The reaction is probably as follows:

(1) $C_6H_5.OH.CO_2H + HNO_3 + H_2SO_4 =$

$C_6H_4(NO_2).OH.CO_2H + H_2SO_4 + H_2O.$

2. Subsequently when zinc sulphide is added the hydrogen sulphide liberated reduces the nitro salicylic acid to amido salicylic acid, as follows:

(2) $C_6H_4(NO_2).OH.CO_2H + 3H_2S + H_2SO_4 =$

$C_6H_4(NH_2).OH.CO_2H + 3S + 2H_2O + H_2SO_4.$

3. The strong sulphuric acid and heat on the amido salicylic acid breaks it up and there is formed ammonium sulphate, carbonic acid, sulphur dioxide and water, as follows:

(3) $2C_6H_4(NH_2).OH.CO_2H + 28H_2SO_4 =$

$(NH_4)_2SO_4 + 14CO_2 + 27SO_2 + 32H_2O.$

Similar reaction probably occurs when benzoic acid or phenol is used, but either nitro compounds are not as readily formed or they are not as easily converted into amido compounds, and probably the heat caused by the reaction when phenol is used is the cause of the loss of some nitric acid. Furthermore, phenol and benzoic acid do not break up as easily in the final reaction and therefore it takes longer to complete the oxidation than when salicylic acid

is used.

Other nitro and amido forming compounds might be substituted for salicylic acid, but by the use of salicylic acid, the method is so simple and accurate that it is doubtful whether any substance other than salicylic acid would improve the method.

Recently, the writer has had other substances under observation. Pure potassium nitrate, using gallic acid in the place of salicylic acid, gave 6.68 % nitrogen; pyrogallic acid, 8.21 %; phenol, 13.62 %; benzaldehyde, 13.62 %; phenyl salicylate, 13.72 %. It is interesting to note that phenyl salicylate gave satisfactory results. The oxidation, however, is not as rapid as when salicylic acid is used.

For ease, manipulation and rapidity of work, and accuracy of results, the salicylic acid method is to be recommended.

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